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(54) **PROPYLENE POLYMER, MOLDED OBJECT THEREOF, AND PROCESS FOR PRODUCING
PROPYLENE POLYMER**

(57) The propylene polymer of the invention is transparent and has good low-temperature heat-sealability and scratch resistance, and is favorable to wrapping and packaging films. (1) The polymer has a melting point, T_m (°C), measured through differential scanning calorimetry, of $110 \leq T_m \leq 140$; (2) its heat of fusion ΔH (J/

g) and melting point T_m (°C) satisfy $\Delta H \geq 0.45 \times T_m + 22$; (3) the half-value width T_h (°C) of the peak top of its elution curve obtained in programmed-temperature fractionation is $T_h \leq 5$; and (4) its intrinsic viscosity $[\eta]$ (d/g) measured in a solvent of tetralin at 135°C falls between 0.5 and 5.

Description

TECHNICAL FIELD

5 [0001] The present invention relates to a propylene polymer and its moldings, and also to a method for producing propylene polymers. Precisely, the invention relates to a propylene polymer of which the advantages are that its modulus of elasticity is well balanced with its melting point, that its low-temperature moldability and workability is good and that it has well-balanced mechanical strength; and relates to moldings obtained by molding the polymer; and also relates to a method for producing such propylene polymers. As having good low-temperature heat-sealability, good transparency, good scratch resistance and good mechanical strength, the propylene polymer of the invention is suitable to wrapping or packaging films.

BACKGROUND ART

15 [0002] Of polyolefins, polypropylene is inexpensive and has excellent physical properties, and its applications cover various fields including, for example, wrapping or packaging films, etc. For wrapping or packaging films, polypropylene must be modified to have improved low-temperature heat-sealability, as its melting point is relatively high. One general technique heretofore employed to meet the requirement comprises copolymerizing propylene with ethylene or with an α -olefin having from 4 to 20 carbon atoms in the presence of a so-called Ziegler-Natta catalyst that comprises a titanium compound or a titanium compound held on a magnesium compound, and an organoaluminium compound.

20 [0003] However, it is known that the low-temperature heat-sealability of wrapping or packaging films of such a propylene- α -olefin copolymer produced in that manner is not satisfactory though the transparency and the scratch resistance thereof are better than those of films of low-density polyethylene (Japanese Patent No. 268562., Japanese Patent Laid-Open Nos. 241439/1997, 255812/1990). If the α -olefin content of the copolymer is increased so as to further improve the low-temperature heat-sealability of the copolymer, it involves some problems in that the composition distribution of the copolymer is broadened and the molecular weight thereof is lowered, and, as a result, the solvent-soluble content of the copolymer increases and the blocking resistance thereof is thereby lowered. Another problem is that the haze of the copolymer films increases, and the transparency thereof lowers.

30 [0004] On the other hand, it is reported that a metallocene catalyst is effective for producing polyolefins having a narrow molecular weight distribution (J. Polym. Sci., Polym. Chem., Ed. 23, 2117 (1985)). Having tried a metallocene catalyst, however, no one has succeeded in producing propylene polymers having well balanced low-temperature heat-sealability and mechanical strength. This is the current situation in the art.

35 [0005] The present invention is to provide a propylene polymer of which the advantages are that its modulus of elasticity is well balanced with its melting point, that its low-temperature moldability and workability is good and that it has well-balanced mechanical strength; and to provide moldings of the polymer and a method for producing the polymer.

DISCLOSURE OF THE INVENTION

40 [0006] We, the present inventors have assiduously studied so as to attain the above-mentioned object, and, as a result, have found that a propylene polymer of which the melting point and the enthalpy of fusion satisfy a specific relationship and of which the half-value width of the peak top of the elution curve obtained in programmed-temperature fractionation falls within a specific range attains the object. On the basis of this finding, we have completed the present invention. Specifically, the invention provides a propylene polymer and its moldings mentioned below, and provides a method for producing the propylene polymer also mentioned below.

45 1. A propylene polymer of which the heat of fusion ΔH (J/g) and the melting point T_m ($^{\circ}\text{C}$) measured through differential scanning calorimetry satisfy the following relationship:

$$\Delta H \geq 0.45 \times T_m + 22.$$

50 2. The propylene polymer of above 1, which has the following properties (1), (2) and (3):

- 55 (1) Its melting point T_m ($^{\circ}\text{C}$) measured through differential scanning calorimetry is $110 \leq T_m \leq 140$;
 (2) The half-value width T_h ($^{\circ}\text{C}$) of the peak top of its elution curve obtained in programmed-temperature fractionation is $T_h \leq 5$;
 (3) Its intrinsic viscosity $[\eta]$ (dL/g) measured in a solvent of tetralin at 135°C falls between 0.5 and 5.

3. The propylene polymer of above 2, of which the melting point T_m ($^{\circ}\text{C}$) measured through differential scanning calorimetry is $120 \leq T_m \leq 140$.

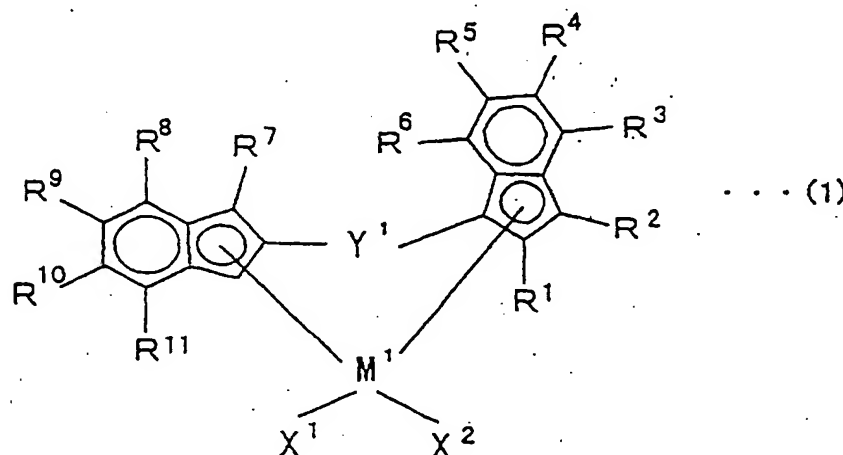
4. The propylene polymer of above 2, of which the melting point T_m ($^{\circ}\text{C}$) measured through differential scanning calorimetry is $120 \leq T_m \leq 135$.

5. The propylene polymer of any of above 1 to 4, which is a propylene homopolymer having an isotactic pentad fraction [mmmm] of from 65 to 85 mol%.

6. The propylene polymer of any of above 1 to 4, which is a propylene homopolymer having an isotactic pentad fraction [mmmm] of from 70 to 80 mol%.

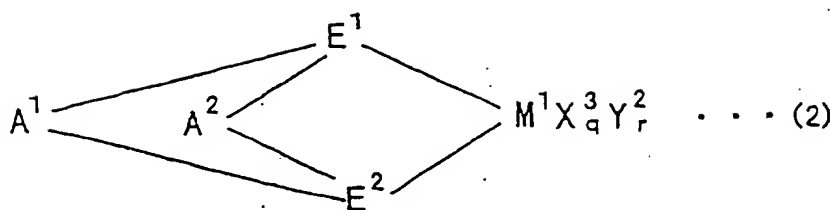
7. A molding obtained by molding the propylene polymer of any of above 1 to 6.

8. A method for producing the propylene polymer of any of above 1 to 6, which comprises polymerizing propylene or propylene with ethylene and/or an α -olefin having from 4 to 20 carbon atoms, in the presence of an olefin polymerization catalyst that contains (A) a transition metal compound of the Group 4 of the Periodic Table represented by the following general formula (1), and (B) at least one selected from (B-1) aluminiumoxy compounds and (B-2) ionic compounds capable of reacting with the transition metal compound to give cations:



wherein R^1 to R^{11} , and X^1 and X^2 each independently represent a hydrogen atom, a halogen atom, a hydrocarbon group having from 1 to 20 carbon atoms, a halogen-containing hydrocarbon group having from 1 to 20 carbon atoms, a silicon-containing group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group, or a phosphorus-containing group; R^3 and R^4 , and R^8 and R^9 may be bonded to each other to form a ring; Y^1 is a divalent crosslinking group that crosslinks the two ligands, representing any of a hydrocarbon group having from 1 to 20 carbon atoms, a halogen-containing hydrocarbon group having from 1 to 20 carbon atoms, a silicon-containing group, a germanium-containing group, a tin-containing group, $-\text{O}-$, $-\text{CO}-$, $-\text{S}-$, $-\text{SO}_2-$, $-\text{NR}^{12}-$, $-\text{PR}^{12}-$, $-\text{P}(\text{O})\text{R}^{12}-$, $-\text{BR}^{12}-$ or $-\text{AlR}^{12}-$; R^{12} represents a hydrogen atom, a halogen atom, a hydrocarbon group having from 1 to 20 carbon atoms, or a halogen-containing hydrocarbon group having from 1 to 20 carbon atoms; M^1 represents titanium, zirconium or hafnium.

9. A method for producing the propylene polymer of any of above 1 to 6, which comprises polymerizing propylene or propylene with ethylene and/or an α -olefin having from 4 to 20 carbon atoms, in the presence of an olefin polymerization catalyst that contains (A) a transition metal compound of the Group 4 of the Periodic Table represented by the following general formula (2), and (B) at least one selected from (B-1) aluminiumoxy compounds and (B-2) ionic compounds capable of reacting with the transition metal compound to give cations:



wherein M^1 represents titanium, zirconium or hafnium; E^1 and E^2 each are a ligand selected from a cyclopentadienyl group, a substituted cyclopentadienyl group, an indenyl group, a substituted indenyl group, a heterocyclopentadienyl group, a substituted heterocyclopentadienyl group, an amido group, a phosphido group, a hydrocarbon group and a silicon-containing group, and they form a crosslinked structure via A^1 and A^2 , and they may be the same or different; X^3 represents a σ -bonding ligand, and a plurality of X^3 's, if any, may be the same or different, and it may be crosslinked with other X^3 , E^1 , E^2 or Y^2 ; Y^2 represents a Lewis base, and a plurality of Y^2 's, if any, may be the same or different, and it may be crosslinked with other Y^2 , E^1 , E^2 or X^3 ; A^1 and A^2 each are a divalent crosslinking group that crosslinks the two ligands, representing any of a hydrocarbon group having from 1 to 20 carbon atoms, a halogen-containing hydrocarbon group having from 1 to 20 carbon atoms, a silicon-containing group, a germanium-containing group, a tin-containing group, $-O-$, $-CO-$, $-S-$, $-SO_2-$, $-NR^{12}-$, $-PR^{12}-$, $-P(O)R^{12}-$, $-BR^{12}-$ or $-AlR^{12}-$; R^{12} represents a hydrogen atom, a halogen atom, a hydrocarbon group having from 1 to 20 carbon atoms, or a halogen-containing hydrocarbon group having from 1 to 20 carbon atoms; and A^1 and A^2 may be the same or different; q is an integer of from 1 to 5, indicating [(valence of M^1)-2]; and r is an integer of from 0 to 3.

10. The method for producing the propylene polymer of above 8 or 9, wherein propylene or propylene with ethylene and/or an α -olefin having from 4 to 20 carbon atoms is polymerized in a vapor phase.

11. The method for producing the propylene polymer of above 8 or 9, wherein propylene or propylene with ethylene and/or an α -olefin having from 4 to 20 carbon atoms is polymerized in the presence of liquid propylene.

BEST MODES OF CARRYING OUT THE INVENTION

[0007] The invention is a propylene polymer and its moldings, and also a method for producing the propylene polymer mentioned above. More precisely, the invention relates to a propylene polymer of which the stereospecificity is on an intermediate level (for example, the stereospecificity of the polymer represented by the isotactic pentad fraction thereof is at most 85 mol%, preferably at most 80 mol%), which is not sticky and has a low melting point, and which is flexible (its tensile modulus falls between 600 and 1,600 MPa, preferably between 700 and 1,200 MPa, more preferably between 800 and 1,100 MPa); and relates to moldings of the polymer and to a method for producing the polymer.

[0008] The invention is described in detail hereinafter.

1. Propylene Polymer:

[0009] The propylene polymer of the invention is such that its heat of fusion ΔH (J/g) and its melting point T_m ($^{\circ}C$) measured through differential scanning calorimetry satisfy the following relationship:

$$\Delta H \geq 0.45 \times T_m + 22.$$

[0010] Polymers not satisfying the requirement lose the balance of melting point and modulus of elasticity thereof, and lose the balance of moldability and workability and mechanical strength thereof. Films of such polymers are unfavorable since the balance of low-temperature heat-sealability and mechanical strength thereof is not good.

[0011] Preferably, ΔH (J/g) and the melting point T_m ($^{\circ}C$) of the propylene polymer of the invention satisfy the following relationship:

$$\Delta H \geq 0.45 \times T_m + 25.$$

[0012] More preferably, the propylene polymer of the invention has the following properties (1), (2) and (3):

- (1) Its melting point T_m ($^{\circ}\text{C}$) measured through differential scanning calorimetry is $110 \leq T_m \leq 140$;
 (2) The half-value width T_h ($^{\circ}\text{C}$) of the peak top of its elution curve obtained in programmed-temperature fractionation is $T_h \leq 5$;
 (3) Its intrinsic viscosity $[\eta]$ (dl/g) measured in a solvent of tetralin at 135°C falls between 0.5 and 5.

[0013] If not satisfying the above-mentioned requirements, the polymer would hardly attain the object of the invention. For example, the polymer having T_m of lower than 110°C and therefore not satisfying the requirement (1) is inconvenient to the field of medicines and edibles as its products will fuse when boiled for sterilization. The polymer having T_m of higher than 140°C could not be a soft material. If not satisfying the requirement (2), the polymer contains an increased amount of sticky components and its films will be not good. The polymer having $[\eta]$ of smaller than 0.5 dl/g and therefore not satisfying the requirement (3) is not so good as its mechanical strength will be low. The polymer having $[\eta]$ of larger than 5.0 dl/g is also not so good as its moldability will be low.

[0014] Even more preferably, the propylene polymer of the invention has the following properties (1), (2), (3) and (4):

- (1) Its heat of fusion ΔH (J/g) and its melting point T_m ($^{\circ}\text{C}$) measured through differential scanning calorimetry satisfy the following relationship:

$$\Delta H \geq 0.45 \times T_m + 22;$$

- (2) Its melting point T_m ($^{\circ}\text{C}$) measured through differential scanning calorimetry is $120 \leq T_m \leq 135$;
 (3) The half-value width T_h ($^{\circ}\text{C}$) of the peak top of its elution curve obtained in programmed-temperature fractionation is $T_h \leq 5$;
 (4) Its intrinsic viscosity $[\eta]$ (dl/g) measured in a solvent of tetralin at 135°C falls between 0.5 and 5.

[0015] Preferably, T_m ($^{\circ}\text{C}$) of the polymer is $120 \leq T_m \leq 140$, more preferably $120 \leq T_m \leq 135$. Also preferably, $[\eta]$ of the polymer falls between 0.5 and 4 dl/g, more preferably between 1.0 and 3 dl/g.

[0016] The methods for measuring the parameters of the polymer are described in detail in the section of Examples given hereinafter.

[0017] In addition to the above-mentioned requirements, the molecular weight distribution (M_w/M_n) of the polymer measured through gel permeation chromatography is preferably at most 4, more preferably at most 3.5, even more preferably at most 3. If its molecular weight distribution (M_w/M_n) is larger than 4, the polymer will be sticky. Also preferably, the boiling diethyl ether extract of the polymer is at most 5 % by weight. If its extract is larger than 5 % by weight, the polymer will be sticky when formed into films. The method for measuring the boiling diethyl ether extract of the polymer is described in detail in the section of Examples given hereinafter. Also preferably, the peak top temperature T_p of the polymer measured through programmed-temperature fractionation falls between 60 and 95°C . Also preferably, the component of the polymer that is eluted within a temperature range of $T_p \pm 5^{\circ}\text{C}$ accounts for at least 70 % by weight of the polymer.

[0018] The propylene polymer of the invention may be a propylene homopolymer and may also be a copolymer of propylene with ethylene and/or an α -olefin having from 4 to 20 carbon atoms (the copolymer is hereinafter referred to as a propylene copolymer). The α -olefin having from 4 to 20 carbon atoms includes 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicosene, etc. In the invention, one more or more of these may be used.

[0019] For the propylene homopolymer, its isotactic pentad fraction [mmmm] preferably falls between 65 and 85 mol%, more preferably between 70 and 80 mol%. The isotactic pentad fraction referred to herein is meant to indicate the isotactic fraction of the pentad units in the molecular chain of polypropylene, which is measured on the basis of the signals for the methyl groups in the ^{13}C nuclear magnetic resonance spectrum of the polymer according to the proposal of A. Zambelli, et al. described in *Macromolecules*, 6, 925, 1973. The ^{13}C nuclear magnetic resonance spectrometry of the polymer is effected by the use of the following apparatus under the condition mentioned below, based on the peak assignment proposed by A. Zambelli et al. in *Macromolecules*, 8, 687, 1975.

Apparatus: JEOL's JNM-EX400 Model ^{13}C -NMR

Method: proton complete decoupling

Concentration: 220 mg/ml

Solvent: 90/10 (by volume) mixed solvent of 1,2,4-trichlorobenzene and heavy benzene

Temperature: 130°C

Pulse width: 45°

Pulse frequency: 4 seconds

Frequency integration: 10,000 times

[0020] For the propylene copolymer, its comonomer content except propylene is preferably at most 1.0 mol%, in addition to the above-mentioned requirements. Also preferably, the stereospecificity index of the copolymer to be indicated by the isotactic triad fraction [mm] of the propylene moiety of the copolymer falls between 80 and 92 mol%. A larger value of the index means that the copolymer has a higher degree of stereospecificity. The copolymer having a stereospecificity index of smaller than 80 mol% could not be molded well as its elasticity will be too low. The copolymer having a stereospecificity index of larger than 92 mol% will be too hard and could not be flexible. The fraction [mm] can be obtained also through ^{13}C -NMR, like the above-mentioned fraction [mmmm]. The method for measuring them is described in detail in the section of Examples given hereinunder. Preferably, the propylene copolymer has a random structure.

[0021] In ordinary propylene polymerization, the carbon atom on the side of the methylene in one propylene monomer compound first bonds to the active point of the polymerization catalyst used, and the other propylene monomer compounds are then coordinated in order in the same manner as before and are polymerized. This is so-called 1,2-insertion in ordinary propylene polymerization. Rarely, however, 2,1-insertion or 1,3-insertion (abnormal insertion) may occur in propylene polymerization. Preferably, the 2,1-insertion or 1,3-insertion seldom occurs in the polymerization to give the propylene polymer of the invention. Concretely, the abnormal insertion in the propylene polymerization in the invention preferably satisfies the following relational formula (1):

$$[(m-2,1) + (r-2,1) + (1,3)] \leq 5.0 (\%) \quad (1)$$

wherein (m-2,1) means the meso-2,1 insert content (%) measured through ^{13}C -NMR; (r-2,1) means the racemi-2,1 insert content (%) measured through ^{13}C -NMR; and (1,3) means the 1,3-insert content (%) measured through ^{13}C -NMR.

[0022] More preferably, it satisfies the following relational formula (2):

$$[(m-2,1) + (r-2,1) + (1,3)] \leq 1.0 (\%) \quad (2).$$

[0023] Most preferably, it satisfies the following relational formula (3):

$$[(m-2,1) + (r-2,1) + (1,3)] \leq 0.1 (\%) \quad (3).$$

[0024] If the propylene polymerization does not satisfy the relational formula (1), the crystallinity of the polymer produced will be low beyond expectation, and the polymer will be sticky.

[0025] The insert contents (m-2,1), (r-2,1) and (1,3) are obtained in accordance with Grassi et al's report (*Macromolecules*, 21, 617, 1988) and Busico et al's report (*Macromolecules*, 27, 7538, 1994). Concretely, based on their proposals, the assignment of the spectral peaks for the respective inserts is determined, and each insert content is obtained from the integrated intensity of each peak. Specifically, the value (m-2,1) is the meso-2,1 insert content (%) of the polymer analyzed, which is calculated from the ratio of the integrated intensity of the peak assigned to the $\text{P}\alpha$, γ -thermo that appears at around 17.2 ppm, to the integrated intensity of the peaks appearing in the total methyl-carbon region. The value (r-2,1) is the racemi-2,1 insert content (%) of the polymer analyzed, which is calculated from the ratio of the integrated intensity of the peak assigned to the $\text{P}\alpha$, γ -thermo that appears at around 15.0 ppm, to the integrated intensity of the peaks appearing in the total methyl carbon region. The value (1,3) is the 1,3-insert content (%) of the polymer analyzed, which is calculated from the ratio of the integrated intensity of the peak assigned to the $\text{T}\beta$, G+ that appears at around 31.0 ppm, to the integrated intensity of the peaks appearing in the total methyl carbon region.

[0026] In ^{13}C -NMR spectrometry of the propylene polymer of the invention, it is more desirable that no peak assigned to the molecular chain terminal (n-butyl group) of the polymer derived from the 2,1-insertion appears in the spectral chart. For the molecular chain terminal derived from the 2,1-insertion, the 2,1-insert content of the polymer is calculated in accordance with Jungling et al's report (*J. Polym. Sci.: Part A: Polym. Chem.*, 33, 1305, 1995). Concretely, the assignment of the peak for the 2,1-insertion in the ^{13}C -NMR chart of the polymer is determined, and the insert content is calculated from the integrated intensity of the peak. For isotactic polypropylene, the peak appearing at around 18.9 ppm is assigned to the carbon atom of the terminal methyl group of the n-butyl group. ^{13}C -NMR to determine the abnormal insertion and the molecular chain terminal of the polymer may be effected by the use of the above-mentioned apparatus under the condition also mentioned above.

2. Method for Producing Propylene Polymer:

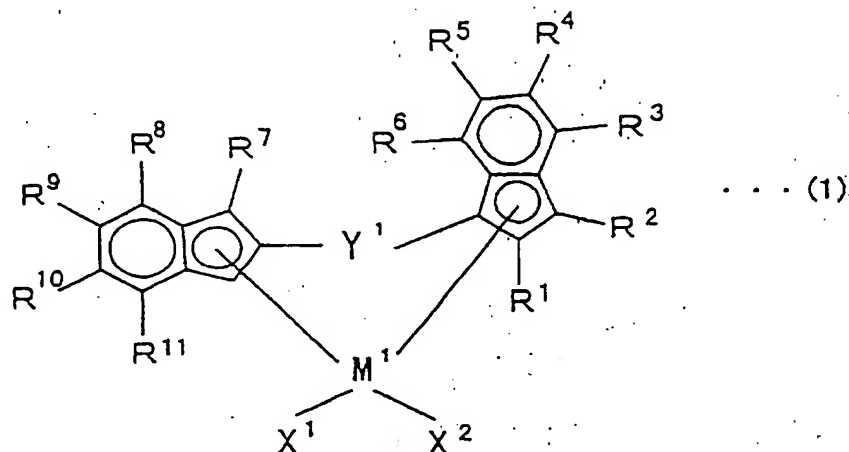
[0027] For producing the propylene polymer of the invention, propylene or propylene with ethylene and/or an α -olefin having from 4 to 20 carbon atoms is polymerized in the presence of an olefin polymerization catalyst that contains (A) a transition metal compound of the Group 4 of the Periodic Table, and (B) at least one selected from (B-1) aluminiumoxy compounds and (B-2) ionic compounds capable of reacting with the transition metal compound to give cations.

[0028] First described are the constituent components of the olefin polymerization catalyst to be used in the invention, and the method for producing the catalyst.

[0029] The component (A) is a transition metal compound of the Group 4 of the Periodic Table, which is selected from the following group A.

[0030] The group A includes the following (A-1) and (A-2): (A-1):

[0031] This is a transition metal compound of the Group 4 of the Periodic Table represented by the following general formula (1):



wherein R^1 to R^{11} , and X^1 and X^2 each independently represent a hydrogen atom, a halogen atom, a hydrocarbon group having from 1 to 20 carbon atoms, a halogen-containing hydrocarbon group having from 1 to 20 carbon atoms, a silicon-containing group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group, or a phosphorus-containing group; R^3 and R^4 , and R^8 and R^9 may be bonded to each other to form a ring; Y^1 is a divalent crosslinking group that crosslinks the two ligands, representing any of a hydrocarbon group having from 1 to 20 carbon atoms, a halogen-containing hydrocarbon group having from 1 to 20 carbon atoms, a silicon-containing group, a germanium-containing group, a tin-containing group, $-O-$, $-CO-$, $-S-$, $-SO_2-$, $-NR^{12}-$, $-PR^{12}-$, $-P(O)R^{12}-$, $-BR^{12}-$ or $-AlR^{12}-$; R^{12} represents a hydrogen atom, a halogen atom, a hydrocarbon group having from 1 to 20 carbon atoms, or a halogen-containing hydrocarbon group having from 1 to 20 carbon atoms; M^1 represents titanium, zirconium or hafnium.

[0032] The transition metal compound is a single-crosslinked complex.

[0033] In formula (1), the halogen atom for R^1 to R^{11} , and X^1 and X^2 includes chlorine, bromine, fluorine and iodine atoms. The hydrocarbon group having from 1 to 20 carbon atoms includes an alkyl group such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-hexyl and n-decyl groups; an aryl group such as phenyl, 1-naphthyl and 2-naphthyl groups; and an aralkyl group such as benzyl group. The halogen-containing hydrocarbon group having from 1 to 20 carbon atoms includes the above-mentioned hydrocarbon groups of which at least one hydrogen atom is substituted with a halogen atom, such as trifluoromethyl group. The silicon-containing group includes trimethylsilyl and dimethyl(t-butyl)silyl groups; the oxygen-containing group includes methoxy and ethoxy groups; the sulfur-containing group includes thiol and sulfonic acid groups; the nitrogen-containing group includes dimethylamino group; the phosphorus-containing group includes phenylphosphine group. R^3 and R^4 , and R^8 and R^9 may be bonded to each other to form a ring such as fluorene. For specific examples of R^3 and R^4 , and R^8 and R^9 bonding to each other, referred to are the groups mentioned above but excepting hydrogen atom. For R^3 and R^9 , preferred are a hydrogen atom and an alkyl group having at most 6 carbon atoms; more preferred are a hydrogen atom, a methyl group, an ethyl group, an isopropyl group, and a cyclohexyl group; and even more preferred is a hydrogen atom. For R^3 , R^4 , R^8 and R^9 , preferred

is an alkyl group having at most 6 carbon atoms; more preferred are a methyl group, an ethyl group, an isopropyl group and a cyclohexyl group; and even more preferred is an isopropyl group. Preferably, R^4 , R^5 , R^7 , R^9 and R^{10} are all hydrogen atoms. More preferably, R^1 is an alkyl group and not a hydrogen atom, and R^7 is a hydrogen atom. For X^1 and X^2 , preferred are a halogen atom, a methyl group, an ethyl group and a propyl group. Specific examples of Y^1 are methylene, ethylene, ethylidene, isopropylidene, cyclohexylidene, 1,2-cyclohexylene, dimethylsilylene, tetramethyldisilylene, dimethylgermylene, methylborylidene ($CH_3-B=$), methylaluminumidene ($CH_3-Al=$), phenylphosphylidene ($Ph-P=$), phenylphosphorylidene ($PhPO=$), 1,2-phenylene, vinylene ($-CH=CH-$), vinylidene ($CH_2=C=$), methylimido, oxygen ($-O-$), sulfur ($-S-$). of these, preferred are methylene, ethylene, ethylidene and isopropylidene for more favorably attaining the object of the invention.

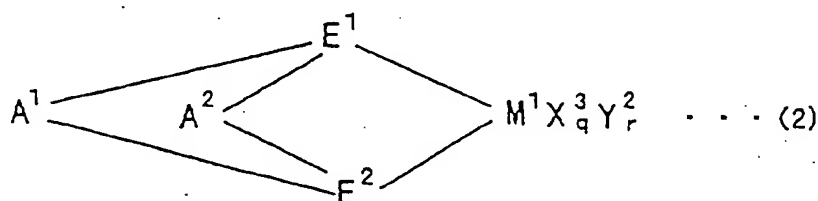
[0034] M^1 indicates titanium, zirconium or hafnium, and is preferably hafnium.

[0035] Specific examples of the transition metal compound of formula (1) are 1,2-ethanediyl(1-(2-isobutylindenyl))(2-indenyl)hafnium dichloride, 1,2-ethanediyl(1-(2-butylindenyl))(2-indenyl)hafnium dichloride, 1,2-ethanediyl(1-(2-butylindenyl))(2-(4,7-dimethylindenyl))hafnium dichloride, 1,2-ethanediyl(1-(2-isopropylindenyl))(2-(4,7-dimethylindenyl))hafnium dichloride, 1,2-ethanediyl(1-(2-isopropylindenyl))(2-(4,7-diisopropylindenyl))hafnium dichloride; dimethylsilylene(1-(2-isobutylindenyl))(2-indenyl)hafnium dichloride, dimethylsilylene(1-(2-butylindenyl))(2-indenyl)hafnium dichloride, dimethylsilylene(1-(2-butylindenyl))(2-(4,7-dimethylindenyl))hafnium dichloride, methylsilylene(1-(2-isopropylindenyl))(2-(4,7-dimethylindenyl))hafnium dichloride, methylsilylene(1-(2-isopropylindenyl))(2-(4,7-diisopropylindenyl))hafnium dichloride; 1,3-propanediyl(1-(2-isopropylindenyl))(2-indenyl)hafnium dichloride, 1,3-propanediyl(1-(2-isobutylindenyl))(2-indenyl)hafnium dichloride, 1,3-propanediyl(1-(2-butylindenyl))(2-indenyl)hafnium dichloride, 1,3-propanediyl(1-(2-butylindenyl))(2-(4,7-dimethylindenyl))hafnium dichloride, 1,3-propanediyl(1-(2-isopropylindenyl))(2-(4,7-diisopropylindenyl))hafnium dichloride; 1,2-ethanediyl(1-(4,7-diisopropylindenyl))(2-(4,7-diisopropylindenyl))hafnium dichloride, 1,2-ethanediyl(9-fluorenyl)(2-(4,7-diisopropylindenyl))hafnium dichloride, isopropylidene(1-(4,7-diisopropylindenyl))(2-(4,7-diisopropylindenyl))hafnium dichloride, 1,2-ethanediyl(1-(4,7-dimethylindenyl))(2-(4,7-diisopropylindenyl))hafnium dichloride, 1,2-ethanediyl(9-fluorenyl)(2-(4,7-dimethylindenyl))hafnium dichloride, isopropylidene(1-(4,7-dimethylindenyl))(2-(4,7-diisopropylindenyl))hafnium dichloride, 1,2-ethanediyl(2-indenyl)(1-(2-isopropylindenyl))hafnium dichloride, dimethylsilylene-(2-indenyl)(1-(2-isopropylindenyl))hafnium dichloride; and also their derivatives derived from the compounds by substituting the hafnium therein with zirconium or titanium. However, these are not limitative.

[0036] The transition metal compound of formula (1) may be produced, for example, according to the method described in the applicant's own prior patent application, Japanese Patent Laid-Open No. 130807/1999. For the component (A-1), two or more of the transition metal compounds may be combined. (A-2):

[0037] This is a transition metal compound of Group 4 of the Periodic Table represented by the following general formula

(2):



wherein M^1 represents titanium, zirconium or hafnium; E^1 and E^2 each are a ligand selected from a cyclopentadienyl group, a substituted cyclopentadienyl group, an indenyl group, a substituted indenyl group, a heterocyclopentadienyl group, a substituted heterocyclopentadienyl group, an amido group, a phosphido group, a hydrocarbon group and a silicon-containing group, and they form a crosslinked structure via A^1 and A^2 , and they may be the same or different; X^3 represents a σ -bonding ligand, and a plurality of X^3 's, if any, may be the same or different, and it may be crosslinked with other X^3 , E^1 , E^2 or Y^2 ; Y^2 represents a Lewis base, and a plurality of Y^2 's, if any, may be the same or different, and it may be crosslinked with other Y^2 , E^1 , E^2 or X^3 ; A^1 and A^2 each are a divalent crosslinking group that crosslinks the two ligands, representing any of a hydrocarbon group having from 1 to 20 carbon atoms, a halogen-containing

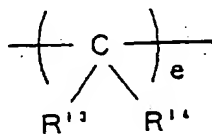
hydrocarbon group having from 1 to 20 carbon atoms, a silicon-containing group, a germanium-containing group, a tin-containing group, -O-, -CO-, -S-, -SO₂-, -NR¹²-, -PR¹²-, -P(O)R¹²-, -BR¹²- or -AlR¹²-; R¹² represents a hydrogen atom, a halogen atom, a hydrocarbon group having from 1 to 20 carbon atoms, or a halogen-containing hydrocarbon group having from 1 to 20 carbon atoms; and A¹ and A² may be the same or different; q is an integer of from 1 to 5, indicating [(valence of M¹)-2]; and r is an integer of from 0 to 3.

[0038] In the transition metal compound of formula (2) (this is hereinafter referred to as a double-crosslinked complex), M¹ represents titanium, zirconium or hafnium, and is preferably zirconium or hafnium. E¹ and E² each are, as so mentioned hereinabove, a ligand selected from a cyclopentadienyl group, a substituted cyclopentadienyl group, an indenyl group, a substituted indenyl group, a heterocyclopentadienyl group, a substituted heterocyclopentadienyl group, an amido group (-N<), a phosphido group (-P<), a hydrocarbon group [>CR-, >C<] and a silicon-containing group [>SiR-, >Si<] (in which R is a hydrogen atom, or a hydrocarbon group having from 1 to 20 carbon atoms, or a hetero atom-containing group), and they form a crosslinked structure via A¹ and A². E¹ and E² may be the same or different. For E¹ and E², preferred are a cyclopentadienyl group, a substituted cyclopentadienyl group, an indenyl group, and a substituted indenyl group.

[0039] Specific examples of the σ-bonding ligand for X³ are a halogen atom, a hydrocarbon group having from 1 to 20 carbon atoms, an alkoxy group having from 1 to 20 carbon atoms, an aryloxy group having from 6 to 20 carbon atoms, an amido group having from 1 to 20 carbon atoms, a silicon-containing group having from 1 to 20 carbon atoms, a phosphido group having from 1 to 20 carbon atoms, a sulfido group having from 1 to 20 carbon atoms, and an acyl group having from 1 to 20 carbon atoms. A plurality of X³s, if any in formula (2), may be the same or different, and X³ may be crosslinked with other X³, E¹, E² or Y².

[0040] Specific examples of the Lewis base for Y² are amines, ethers, phosphines, and thioethers. A plurality of Y²s, if any in formula (2), may be the same or different, and Y² may be crosslinked with other Y², E¹, E² or X³.

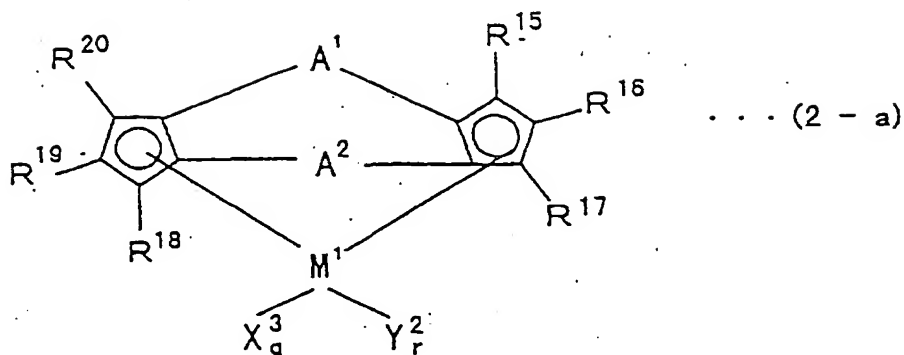
[0041] Preferably, at least one crosslinking group for A¹ and A² is a hydrocarbon group having at least one carbon atom. For example, the crosslinking group is represented by a general formula:



wherein R¹³ and R¹⁴ each represent a hydrogen atom, or a hydrocarbon group having from 1 to 20 carbon atoms, and they may be the same or different, and may be bonded to each other to form a cyclic structure; and e indicates an integer of from 1 to 4.

[0042] Specific examples of the group are a methylene group, an ethylene group, an ethylidene group, a propylidene group, an isopropylidene group, a cyclohexylidene group, a 1,2-cyclohexylene group, and a vinylidene group (CH₂=C=). Of these, preferred are a methylene group, an ethylene group and an isopropylidene group. A¹ and A² may be the same or different.

[0043] In the transition metal compound of formula (2) where E¹ and E² each are a cyclopentadienyl group, a substituted cyclopentadienyl group, an indenyl group or a substituted indenyl group, the bond of the crosslinking group of A¹ and A² may be in the form of a double-crosslinking mode of (1,1') (2,2') or in the form of a double-crosslinking mode of (1,2')(2,1'). Of the transition metal compounds of formula (2), preferred are those having a double-crosslinked bis-cyclopentadienyl derivative as the ligand of the following general formula (2-a):



[0044] In formula (2-a), M¹, A¹, A², q and r have the same meanings as above. X³ represents a σ-bonding ligand, and a plurality of X³'s, if any, may be the same or different, and it may be crosslinked with other X³ or Y². For specific examples of X³, referred to are the same as those mentioned hereinabove for X³ in formula (2). Y² represents a Lewis base, and a plurality of Y²'s, if any, may be the same or different, and it may be crosslinked with other Y² or X³. For specific examples of Y², referred to are the same as those mentioned hereinabove for Y² in formula (2). R¹⁵ to R²⁰ each represent a hydrogen atom, a halogen atom, a hydrocarbon group having from 1 to 20 carbon atoms, a halogen-containing hydrocarbon group having from 1 to 20 carbon atoms, a silicon-containing group, or a hetero atom-containing group, and at least one of them must not be a hydrogen atom. R¹⁵ to R²⁰ may be the same or different, and the neighboring groups of them may be bonded to each other to form a ring. Preferably, the neighboring groups form an indenyl group which is substituted with an aromatic ring bonded thereto.

[0045] In the transition metal compound having such a double-crosslinked biscyclopentadienyl derivative as the ligand, the ligand may be any of a (1,1')(2,2') double-crosslinked one or a (1,2')(2,1') double-crosslinked one.

[0046] Specific examples of the transition metal compound of formula (2) are (1,1'-ethylene)(2,2'-ethylene)-bis(indenyl)zirconium dichloride, (1,2'-ethylene)(2,1'-ethylene)-bis(indenyl)zirconium dichloride, (1,1'-methylene)(2,2'-methyleylene)-bis(indenyl)zirconium dichloride, (1,2'-methylene)(2,1'-methylene)-bis(indenyl)zirconium dichloride, (1,1'-isopropylidene)(2,2'-isopropylidene)-bis(indenyl)zirconium dichloride, (1,2'-isopropylidene)(2,1'-isopropylidene)-bis(indenyl)zirconium dichloride, (1,1'-ethylene)(2,2'-ethylene)-bis(3-methylindenyl)zirconium dichloride, (1,2'-ethylene)(2,1'-ethylene)-bis(3-methylindenyl)zirconium dichloride, (1,1'-ethylene)(2,2'-ethylene)-bis(4,5-benzoidindenyl)zirconium dichloride, (1,2'-ethylene)(2,1'-ethylene)-bis(4,5-benzoidindenyl)zirconium dichloride, (1,1'-ethylene)(2,2'-ethylene)-bis(4-isopropylindenyl)zirconium dichloride, (1,2'-ethylene)(2,1'-ethylene)-bis(4-isopropylindenyl)zirconium dichloride, (1,1'-ethylene)(2,2'-ethylene)-bis(5,6-dimethylindenyl)zirconium dichloride, (1,2'-ethylene)(2,1'-ethylene)-bis(5,6-dimethylindenyl)zirconium dichloride, (1,1'-ethylene)(2,2'-ethylene)-bis(4,7-diisopropylindenyl)zirconium dichloride, (1,2'-ethylene)(2,1'-ethylene)-bis(4,7-diisopropylindenyl)zirconium dichloride, (1,1'-ethylene)(2,2'-ethylene)-bis(4-phenylindenyl)zirconium dichloride, (1,2'-ethylene)(2,1'-ethylene)-bis(4-phenylindenyl)zirconium dichloride, (1,1'-ethylene)(2,2'-ethylene)-bis(3-methyl-4-isopropylindenyl)zirconium dichloride, (1,2'-ethylene)(2,1'-ethylene)-bis(3-methyl-4-isopropylindenyl)zirconium dichloride, (1,1'-ethylene)(2,2'-ethylene)-bis(5,6-benzoidindenyl)zirconium dichloride, (1,2'-ethylene)(2,1'-ethylene)-bis(5,6-benzoidindenyl)zirconium dichloride, (1,1'-ethylene)(2,2'-isopropylidene)-bis(indenyl)zirconium dichloride, (1,2'-ethylene)(2,1'-isopropylidene)-bis(indenyl)zirconium dichloride, (1,1'-isopropylidene)(2,2'-ethylene)-bis(indenyl)zirconium dichloride, (1,2'-methylene)(2,1'-ethylene)-bis(indenyl)zirconium dichloride, (1,1'-methylene)(2,2'-ethylene)-bis(indenyl)zirconium dichloride, (1,1'-ethylene)(2,2'-methylene)-bis(indenyl)zirconium dichloride, (1,1'-methylene)(2,2'-isopropylidene)-bis(indenyl)zirconium dichloride, (1,2'-methylene)(2,1'-isopropylidene)-bis(indenyl)zirconium dichloride, (1,1'-isopropylidene)(2,2'-methylene)-bis(indenyl)zirconium dichloride, (1,1'-methylene)(2,2'-methylene)(3-methylcyclopentadienyl)(cyclopentadienyl)zirconium dichloride, (1,1'-isopropylidene)(2,2'-isopropylidene)(3-methylcyclopentadienyl)(cyclopentadienyl)zirconium dichloride, (1,1'-propylidene)(2,2'-propylidene)(3-methylcyclopentadienyl)(cyclopentadienyl)zirconium dichloride, (1,1'-ethylene)(2,2'-methylene)-bis(3-methylcyclopentadienyl)zirconium dichloride, (1,1'-methylene)(2,2'-ethylene)-bis(3-methylcyclopentadienyl)zirconium dichloride, (1,1'-isopropylidene)(2,2'-ethylene)-bis(3-methylcyclopentadienyl)zirconium dichloride, (1,1'-ethylene)(2,2'-isopropylidene)-bis(3-methylcyclopentadienyl)zirconium dichloride, (1,1'-methylene)(2,2'-methylene)-bis(3-methylcyclopentadienyl)zirconium dichloride, (1,1'-ethylene)(2,2'-isopropylidene)-bis(3-methylcyclopentadienyl)zirconium dichloride, (1,1'-methylene)(2,2'-isopropylidene)-bis(3-methylcyclopentadienyl)zirconium dichloride, (1,1'-isopropylidene)(2,2'-isopropylidene)-bis(3-methylcyclopentadienyl)zirconium dichloride, (1,1'-ethylene)(2,2'-methylene)-bis(3,4-dimethylcyclopentadienyl)zirconium dichloride, (1,1'-ethylene)(2,2'-isopropylidene)

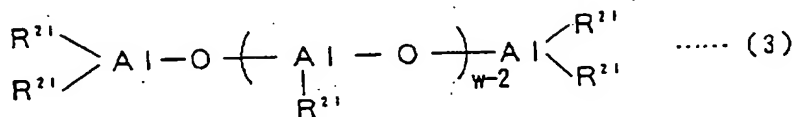
dene)-bis(3,4-dimethylcyclopentadienyl)zirconium dichloride, (1,1'-methylene)(2,2'-methylene)-bis(3,4-dimethylcyclopentadienyl)zirconium dichloride, (1,1'-methylene)(2,2'-isopropylidene)-bis(3,4-dimethylcyclopentadienyl)zirconium dichloride, (1,1'-isopropylidene)(2,2'-isopropylidene)-bis(3,4-dimethylcyclopentadienyl)zirconium dichloride, (1,2'-ethylene)(2,1'-methylene)-bis(3-methylcyclopentadienyl)zirconium dichloride, (1,2'-ethylene)(2,1'-isopropylidene)-bis(3-methylcyclopentadienyl)zirconium dichloride, (1,2'-methylene)(2,1'-methylene)-bis(3-methylcyclopentadienyl)zirconium dichloride, (1,2'-methylene)(2,1'-isopropylidene)-bis(3-methylcyclopentadienyl)zirconium dichloride, (1,2'-isopropylidene)(2,1'-isopropylidene)-bis(3-methylcyclopentadienyl)zirconium dichloride, (1,2'-ethylene)(2,1'-methylene)-bis(3,4-dimethylcyclopentadienyl)zirconium dichloride, (1,2'-ethylene)(2,1'-isopropylidene)-bis(3,4-dimethylcyclopentadienyl)zirconium dichloride, (1,2'-methylene)(2,1'-methylene)-bis(3,4-dimethylcyclopentadienyl)zirconium dichloride, (1,2'-isopropylidene)(2,1'-isopropylidene)-bis(3,4-dimethylcyclopentadienyl)zirconium dichloride, (1,2'-ethylene)(2,1'-ethylene)-bis(5,5-phenylindenyl)zirconium dichloride, (1,2'-ethylene)(2,1'-ethylene)-bis(5,6-phenylindenyl)zirconium dichloride, (1,2'-ethylene)(2,1'-ethylene)-bis(6,6-phenylindenyl)zirconium dichloride, and their derivatives derived from the compounds by substituting the zirconium therein with titanium or hafnium; as well as dimethylsilylene(1-(2-methyl-4,5-benzoindenyl))(2-indenyl)zirconium dichloride, dimethylsilylene(1-(2-ethyl-4,5-benzoindenyl))(2-indenyl)zirconium dichloride, dimethylsilylene(1-(2-butyl-4,5-benzoindenyl))(2-indenyl)zirconium dichloride, dimethylsilylene(1-(2-methyl-4,5-benzoindenyl))(2-4,7-dimethylindenyl)zirconium dichloride, dimethylsilylene(1-(2-ethyl-4,5-benzoindenyl))(2-4,7-dimethylindenyl)zirconium dichloride, diphenylsilylene(1-(2-methyl-4,5-benzoindenyl))(2-indenyl)zirconium dichloride, diphenylsilylene(1-(2-ethyl-4,5-benzoindenyl))(2-indenyl)zirconium dichloride, diphenylsilylenesilylene(1-(2-butyl-4,5-benzoindenyl))(2-indenyl)zirconium dichloride, diphenylsilylene(1-(2-methyl-4,5-benzoindenyl))(2-4,7-dimethylindenyl)zirconium dichloride, diphenylsilylene(1-(2-ethyl-4,5-benzoindenyl))(2-4,7-dimethylindenyl)zirconium dichloride, and their derivatives with hafnium and not zirconium. Needless-to-say, the invention is not limited to these compounds. For the component (A-2), two or more of these transition metal compounds may be combined.

[0047] For the component (A) of the olefin polymerization catalyst to be used in the invention, preferred is the component (A-1).

[0048] Next described is the component (B).

[0049] The component (B) for use in the invention is at least one selected from (B-1) aluminiumoxy compounds and (B-2) ionic compounds capable of reacting with the transition metal compound to give cations.

[0050] The aluminiumoxy compounds for the component (B-1) include linear aluminoxanes of the following general formula (3):



wherein R^{21} represents a hydrocarbon group, such as an alkyl, alkenyl, aryl, arylalkyl or the like group having from 1 to 20, preferably from 1 to 12 carbon atoms, or a halogen atom; w indicates a degree of mean polymerization, and is an integer generally falling between 2 and 50, preferably between 2 and 40; and plural R^{21} 's may be the same or different, and cyclic aluminoxanes of the following general formula (4):



wherein R^{21} and w have the same meanings as in formula (3).

[0051] Concretely, they include methylaluminumoxane, ethylaluminumoxane and isobutylaluminumoxane.

[0052] For producing the aluminumoxanes, an alkylaluminum may be contacted with a condensation agent such as water or the like, for which the mode of condensation is not specifically defined and the reactants may be reacted in any ordinary manner. For it, for example, employable is (1) a method comprising dissolving an organoaluminum compound in an organic solvent followed by contacting it with water; (2) a method comprising directly adding an organoaluminum compound to the polymerization system that requires the intended aluminumoxane, followed by adding water thereto; (3) a method comprising reacting an organoaluminum compound with crystal water existing in metal salts and the like or with water having adsorbed by inorganic or organic substances; or (4) a method comprising reacting a tetraalkyldialuminumoxane with a trialkylaluminum and then with water.

[0053] The aluminumoxanes may be insoluble or soluble in hydrocarbon solvents. Preferably, however, they are soluble in hydrocarbon solvents and the residual organoaluminum compound therein measured through $^1\text{H-NMR}$ accounts for at most 10 % by weight, more preferably from 3 to 5 % by weight, even more preferably from 2 to 4 % by weight. One advantage of the aluminumoxanes of that type is that the proportion of the aluminumoxane capable of being held on a carrier (this may be referred to as an on-carrier percentage of the compound) high. Another advantage of the aluminumoxanes soluble in hydrocarbon solvents is that their part not held on a carrier can be recycled. Still another advantage is that they do not require any specific treatment before use since their properties are stable. Still another advantage is that the morphology (including the mean particle size and the particle size distribution) of the polyolefins produced through polymerization in the presence of the aluminumoxane of that type is good. If the residual organoaluminum compound in aluminumoxanes accounts for more than 10 % by weight, it is unfavorable since the on-carrier percentage of the aluminumoxane will decrease and the polymerization activity thereof will thereby decrease.

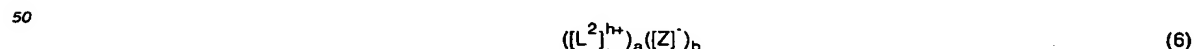
[0054] For obtaining the aluminumoxanes of that type, for example, employable is a method that comprises drying up an aluminumoxane solution to completely remove the solvent from it through distillation to dryness under heat under reduced pressure (this is referred to as a drying-up method). In the drying-up method under heat under reduced pressure, it is desirable that the solvent is evaporated away at a temperature not higher than 80°C , more preferably not higher than 60°C .

[0055] The fraction not soluble in hydrocarbon solvents may be removed from the aluminumoxanes. For removing it, for example, employable is a method that comprises processing the aluminumoxane in a hydrocarbon solvent to lead to spontaneous precipitation of the fraction not soluble in the solvent, followed by removing the insoluble fraction through decantation. Another method comprises removing the insoluble fraction through centrifugation or the like. More preferably, the thus-recovered, soluble fraction is filtered through a G5 glass filter or the like in a nitrogen atmosphere, whereby the insoluble fraction is more completely removed from it. The thus-processed aluminumoxane will have an increased amount of a gelled fraction with the lapse of time. Therefore, it is desirable that the organoaluminumoxane is used within 48 hours after its preparation, more preferably immediately after its preparation. The ratio of the organoaluminumoxane to the hydrocarbon solvent is not specifically defined, but it is desirable that the amount of the organoaluminumoxane falls between 0.5 and 10 moles in terms of the aluminum atom in the compound relative to 1 liter of the hydrocarbon solvent.

[0056] The hydrocarbon solvents include, for example, aromatic hydrocarbons such as benzene, toluene, xylene, cumene, cymene; aliphatic hydrocarbons such as pentane, hexane, heptane, octane, decane, dodecane, hexadecane, octadecane; alicyclic hydrocarbons such as cyclopentane, cyclohexane, cyclooctane, methylcyclopentane; petroleum fractions such as naphtha, kerosene, light gas oil.

[0057] One or more of these aluminumoxanes may be used herein either singly or as combined.

[0058] For the component (B-2), usable are any ionic compounds capable of reacting with the above-mentioned transition metal compound to give cations. Especially preferred are ionic compounds of the following formulae (5) and (6), as they can efficiently form polymerization active points.



wherein L^2 indicates M^2 , $R^{23}R^{24}M^3$, R^{25}_3C or $R^{26}M^3$.

[0059] In formulae (5) and (6), L^1 indicates a Lewis base; $[Z]^-$ indicates a non-coordinating anion $[Z^1]^-$ or $[Z^2]^-$; $[Z^1]^-$ is an anion with a plurality of groups bonded to an element, and it may be represented by $[M^4G^1G^2 \dots G^f]$ wherein M^4 is an element of Groups 5 to 15 of the Periodic Table, preferably an element of Groups 13 to 15 of the Periodic Table; G^1 to G^f each indicate a hydrogen atom, a halogen atom, an alkyl group having from 1 to 20 carbon atoms, a dialkylamino

group having from 2 to 40 carbon atoms, an alkoxy group having from 1 to 20 carbon atoms, an aryl group having from 6 to 20 carbon atoms, an aryloxy group having from 6 to 20 carbon atoms, an alkylaryl group having from 7 to 40 carbon atoms, an arylalkyl group having from 7 to 40 carbon atoms, a halogen-substituted hydrocarbon group having from 1 to 20 carbon atoms, an acyloxy group having from 1 to 20 carbon atoms, an organometalloid group, or a hetero atom-containing hydrocarbon group having from 2 to 20 carbon atoms; and two or more of G¹ to G^f may form a ring; f is an integer, indicating [(valence of the center metal M⁴) + 1]; [Z²]⁻ is a conjugated base of a Brønsted acid, of which the logarithmic number (pKa) of the reciprocal of the acid dissociation constant is not larger than -10, alone or a combination of such a Brønsted acid and a Lewis acid, or is a conjugated base which is generally defined as an ultra-strong acid, and it may be coordinated with a Lewis base; R²² indicates a hydrogen atom, an alkyl group having from 1 to 20 carbon atoms, an aryl group having from 6 to 20 carbon atoms, an alkylaryl group having from 7 to 40 carbon atoms, or an arylalkyl group having from 7 to 40 carbon atoms; R²³ and R²⁴ each indicate a cyclopentadienyl group, a substituted cyclopentadienyl group, an indenyl group, or a fluorenyl group; R²⁵ indicates an alkyl group having from 1 to 20 carbon atoms, an aryl group having from 6 to 20 carbon atoms, an alkylaryl group having from 7 to 40 carbon atoms, or an arylalkyl group having from 7 to 40 carbon atoms; R²⁶ indicates a macrocyclic ligand such as tetraphenylporphyrin or phthalocyanine; h is an integer of from 1 to 3, indicating the ion valence of [L¹ - R²²] or [L²]; a is an integer of at least 1; b = (h × a); M² includes elements of Groups 1 to 3, 11 to 13 and 17 of the Periodic Table; and M³ indicates an element of Groups 7 to 12 of the Periodic Table.

[0060] Specific examples of L¹ are ammonia; amines such as methylamine, aniline, dimethylamine, diethylamine, N-methylaniline, diphenylamine, N,N-dimethylaniline, trimethylamine, triethylamine, tri-n-butylamine, methyldiphenylamine, pyridine, p-bromo-N,N-dimethylaniline, p-nitro-N,N-dimethylaniline; phosphines such as triethylphosphine, triphenylphosphine, diphenylphosphine; thioethers such as tetrahydrothiophene; esters such as ethyl benzoate; and nitriles such as acetonitrile, benzonitrile.

[0061] Specific examples of R²² are a hydrogen atom, a methyl group, an ethyl group, a benzyl group and a trityl group; specific examples of R²³ and R²⁴ are a cyclopentadienyl group, a methylcyclopentadienyl group, an ethylcyclopentadienyl group, and a pentamethylcyclopentadienyl group. Specific examples of R²⁵ are a phenyl group, a p-tolyl group, and a p-methoxyphenyl group. Specific examples of R²⁶ are tetraphenylporphyrin, phthalocyanine, allyl and methallyl. Specific examples of M² are Li, Na, K, Ag, Cu, Br, I, and I₃. Specific examples of M³ are Mn, Fe, Co, Ni, and Zn.

[0062] Specific examples of M⁴ in [M⁴G¹G² ... G^f] for [Z¹]⁻ are B, Al, Si, P, As and Sb. Preferred are B and Al. Specific examples of G¹, G² to G^f are a dialkylamino group such as dimethylamino and diethylamino groups; an alkoxy or aryloxy group such as methoxy, ethoxy, n-butoxy and phenoxy groups; a hydrocarbon group such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-octyl, n-eicosyl, phenyl, p-tolyl, benzyl, 4-t-butylphenyl and 3,5-dimethylphenyl groups; a halogen atom such as fluorine, chlorine, bromine and iodine atoms; a hetero atom-containing hydrocarbon group such as p-fluorophenyl, 3,5-difluorophenyl, pentachlorophenyl, 3,4,5-trifluorophenyl, pentafluorophenyl, 3,5-bis(trifluoromethyl)phenyl, and bis(trimethylsilyl)methyl groups; an organometalloid group such as pentamethylantimonyl, trimethylsilyl, trimethylgermyl, diphenylarsenyl, dicyclohexylantimonyl and diphenylboryl groups.

[0063] Specific examples of the non-coordinating anion, [Z²]⁻, which is a conjugated base of a Brønsted acid having pKa of at most -10 alone or a combination of such a Brønsted acid and a Lewis acid, are trifluoromethanesulfonate anion (CF₃SO₃)⁻, bis(trifluoromethanesulfonyl)methyl anion, bis(trifluoromethanesulfonyl)benzyl anion, bis(trifluoromethanesulfonyl)amido anion, perchlorate anion (ClO₄)⁻, trifluoroacetate anion (CF₃CO₂)⁻, hexafluoroantimonyl anion (SbF₆)⁻, fluorosulfonate anion (FSO₃)⁻, chlorosulfonate anion (ClSO₃)⁻, fluorosulfonate anion/pentafluoroantimonyl (FSO₃/SbF₅)⁻, fluorosulfonate anion/pentafluoroarsenic (FSO₃/AsF₅)⁻, and trifluoromethanesulfonate anion/pentafluoroantimonyl (CF₃SO₃/SbF₅)⁻.

[0064] Specific examples of the compounds for the component (B-2) are triethylammonium tetraphenylborate, tri-n-butylammonium tetraphenylborate, trimethylammonium tetraphenylborate, tetraethylammonium tetraphenylborate, methyl(tri-n-butyl)ammonium tetraphenylborate, benzyl(tri-n-butyl)ammonium tetraphenylborate, dimethyldiphenylammonium tetraphenylborate, trimethyl(methyl)ammonium tetraphenylborate, trimethylanilinium tetraphenylborate, methylpyridinium tetraphenylborate, benzylpyridinium tetraphenylborate, methyl(2-cyanopyridinium) tetraphenylborate, triethylammonium tetrakis(pentafluorophenyl)borate, tri-n-butylammonium tetrakis(pentafluorophenyl)borate, triphenylammonium tetrakis(pentafluorophenyl)borate, tetra-n-butylammonium tetrakis(pentafluorophenyl)borate, tetraethylammonium tetrakis(pentafluorophenyl)borate, benzyl(tri-n-butyl)ammonium tetrakis(pentafluorophenyl)borate, methyldiphenylammonium tetrakis(pentafluorophenyl)borate, triphenyl(methyl)ammonium tetrakis(pentafluorophenyl)borate, methylanilinium tetrakis(pentafluorophenyl)borate, dimethylanilinium tetrakis(pentafluorophenyl)borate, trimethylanilinium tetrakis(pentafluorophenyl)borate, methylpyridinium tetrakis(pentafluorophenyl)borate, benzylpyridinium tetrakis(pentafluorophenyl)borate, methyl(2-cyanopyridinium)tetrakis(pentafluorophenyl)borate, benzyl(2-cyanopyridinium)tetrakis(pentafluorophenyl)borate, methyl(4-cyanopyridinium)tetrakis(pentafluorophenyl)borate, triphenylphosphonium tetrakis(pentafluorophenyl)borate, dimethylanilinium tetrakis[bis(3,5-difluoromethyl)phenyl]borate, ferrocenium tetraphenylborate, silver tetraphenylborate, trityl tetraphenylborate, tetraphenylporphyrin-manganese tetra-

phenylborate, ferrocenium tetrakis(pentafluorophenyl)borate, (1,1'-dimethylferrocenium) tetrakis(pentafluorophenyl) borate, decamethylferrocenium tetrakis(pentafluorophenyl)borate, silver tetrakis(pentafluorophenyl)borate, trityl tetrakis(pentafluorophenyl)borate, lithium tetrakis(pentafluorophenyl)borate, sodium tetrakis(pentafluorophenyl)borate, tetraphenylporphyrin-manganese tetrakis(pentafluorophenyl)borate, silver tetrafluoroborate, silver hexafluorophosphate, silver hexafluoroarsenate, silver perchlorate, silver trifluoroacetate, and silver trifluoromethanesulfonate. For the component (B-2), preferred are the ionic compounds of formula (5).

[0065] For the component (B-2), one or more of the ionic compounds capable of reacting with the transition metal compound of the component (A) to give cations may be used herein either singly or as combined.

[0066] In the olefin polymerization catalyst for use in the invention, the component (B) may be the component (B-1) alone or the component (B-2) alone, or may also be a combination of the components (B-1) and (B-2).

[0067] The catalyst may comprise, as the essential ingredients, the components (A) and (B), or may comprise, as the essential ingredients the components (A) and (B) and an additional component (C) of an organoaluminium compound.

[0068] The organoaluminium compound for the component (C) may be represented by a general formula (7):



wherein R^{27} indicates an alkyl group having from 1 to 10 carbon atoms; Q indicates a hydrogen atom, an alkoxy group having from 1 to 20 carbon atoms, an aryl group having from 6 to 20 carbon atoms, or a halogen atom; and v is an integer of from 1 to 3.

[0069] Specific examples of the compound of formula (7) are trimethylaluminium, triethylaluminium, triisopropylaluminium, triisobutylaluminium, dimethylaluminium chloride, diethylaluminium chloride, methylaluminium dichloride, ethylaluminium dichloride, dimethylaluminium fluoride, diisobutylaluminium hydride, diethylaluminium hydride, and ethylaluminium sesqui-chloride.

[0070] One or more of these organoaluminium compounds may be used herein either singly or as combined.

[0071] Regarding the ratio of the catalyst component (A) and the catalyst component (B) that constitute the polymerization catalyst, the molar ratio of the component (A) to the compound (B-1) for the component (B) preferably falls between 1/1 and 1/10⁶, more preferably between 1/10 and 1/10⁴. If the ratio oversteps the defined range, the catalyst cost per the unit weight of the polymer to be produced will be high, and it is impracticable. The molar ratio of the component (A) to the compound (B-2) for the component (B) preferably falls between 10/1 and 1/100, more preferably between 2/1 and 1/10, to the component (A). If the ratio oversteps the defined range, the catalyst cost per the unit weight of the polymer to be produced will be high, and it is impracticable.

[0072] The molar ratio of the catalyst component (A) to the optional catalyst component (C) preferably falls between 1/1 and 1/20,000, more preferably between 1/5 and 1/2,000, even more preferably between 1/10 and 1/1,000. The catalyst component (C), if used, enhances the polymerization activity per the transition metal of the catalyst. However, if the component (C) is too much, especially overstepping the defined range, the organoaluminium compound used shall be wasted, and will much remain in the polymer produced; but if too small, it will be often unfavorable since the catalyst activity will be poor.

[0073] In the invention, at least one catalyst component may be held on a suitable carrier. The carrier is not specifically defined, and may be any of inorganic oxides, and even other inorganic substances and organic substances. For well controlling the morphology of the polymer to be produced, preferred are inorganic oxide carriers and other inorganic carriers. Concretely, the inorganic oxide carriers include SiO₂, Al₂O₃, MgO, ZrO₂, TiO₂, Fe₂O₃, B₂O₃, CaO, ZnO, BaO, ThO₂, and their mixtures, for example, silica-alumina, zeolite, ferrite, and glass fibers. Of those, especially preferred are SiO₂ and Al₂O₃. The inorganic oxide carriers may contain minor carbonates, nitrates and sulfates. In addition to the carriers mentioned above, also usable herein are other carriers of magnesium compounds of a general formula $MgR^{28}_x X^4_y$, such as MgCl₂ and Mg(OC₂H₅)₂, and their complexes. In the formula, R^{28} represents an alkyl group having from 1 to 20 carbon atoms, an alkoxy group having from 1 to 20 carbon atoms, or an aryl group having from 6 to 20 carbon atoms; X^4 represents a halogen atom, or an alkyl group having from 1 to 20 carbon atoms; x falls between 0 and 2, y falls between 0 and 2, and x + y = 2. Plural R^{28} 's and plural X^4 's may be the same or different. The organic carriers usable herein include polymers such as polystyrenes, styrene-divinylbenzene copolymers, polyethylenes, polypropylenes, substituted polystyrenes, polyarylates; as well as starch and carbon. Preferred carriers for use in the invention are MgCl₂, MgCl(OC₂H₅), Mg(OC₂H₅)₂, SiO₂ and Al₂O₃. The properties of the carriers vary, depending on their type and the method for producing them. The carriers will have a mean pore size generally falling between 1 and 300 μ m, but preferably between 10 and 200 μ m, more preferably between 20 and 100 μ m. If the particle size of the carrier used is too small, the fine powder content of the polymer produced will increase; but if too large, the coarse particles in the polymer will increase, and they lower the bulk density of the polymer and will clog hoppers. The specific surface

area of the carrier may fall generally between 1 and 1,000 m²/g, but preferably between 50 and 500 m²/g; and the pore volume thereof may fall generally between 0.1 to 5 cm³/g, but preferably between 0.3 and 3 cm³/g. If any of the specific surface area and the pore volume of the carrier oversteps the defined range, the catalyst activity will be low. The specific surface area and the pore volume of the carrier may be derived from the volume of the nitrogen gas having been absorbed by the carrier, for example, according to the BET method (see *J. Am. Chem. Soc.*, Vol. 60, p. 309 (1938)). Preferably, the carrier is baked at a temperature falling between 150 and 1,000°C, more preferably between 200 and 800°C, before it is used herein.

[0074] When at least one catalyst component is held on the carrier, it is desirable that at least one of the catalyst component (A) and the catalyst component (B), more preferably both the components (A) and (B) are held thereon for ensuring good morphology control of the polymer to be produced and for ensuring good applicability of the catalyst to vapor-phase polymerization to give the polymer.

[0075] The method for holding at least one of the components (A) and (B) on a carrier such as that mentioned above is not specifically defined. For example, (1) at least one of the components (A) and (B) may be mixed with a carrier; (2) a carrier is first processed with an organoaluminium compound or a halogen-containing silicon compound (e.g., silicon tetrachloride, methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane), and this is then mixed with at least one of the components (A) and (B) in an inert solvent; (3) a carrier is, along with either one or both of the components (A) and (B), reacted with an organoaluminium compound or a halogen-containing silicon compound (e.g., silicon tetrachloride, methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane); (4) the component (A) or (B) is held on a carrier, and this is then mixed with the other component (B) or (A); (5) a product prepared by contacting the components (A) and (B) with each other is mixed with a carrier; or (6) the components (A) and (B) are contacted with each other in the presence of a carrier. In the methods (4), (5) and (6), an organoaluminium compound may be optionally added to the system. The organoaluminium compound may be selected from those for the component (C) mentioned hereinabove.

[0076] In the method (4), (5) and (6), the organoaluminium compound for the component (C) may be optionally added to the system.

[0077] In the invention, the ratio of the component (B-1) to the carrier preferably falls between 1/0.5 and 1/1,000, more preferably between 1/1 and 1/50 by weight; and the ratio of the component (B-2) to the carrier preferably falls between 1/5 and 1/10,000, more preferably between 1/10 and 1/500 by weight. When the catalyst component (B) is a mixture of two or more compounds, it is desirable that the ratio by weight of each compound to the carrier falls within the defined range. The ratio of the component (A) to the carrier preferably falls between 1/5 and 1/10,000, more preferably between 1/10 and 1/500 by weight.

[0078] If the ratio of the component (B) (component (B-1), component (B-2)) to the carrier, or the ratio of the component (A) to the carrier oversteps the defined range, the catalyst activity will be low. The mean particle size of the polymerization catalyst thus prepared herein for use in the invention may fall generally between 2 and 200 µm, but preferably between 10 and 150 µm, more preferably between 20 and 100 µm; and the specific surface area thereof may fall generally between 20 and 1,000 m²/g, but preferably between 50 and 500 m²/g. If the mean particle size of the catalyst is smaller than 2 µm, fine powder in the polymer produced will increase; but if larger than 200 µm, coarse particles therein will increase. If the specific surface area of the catalyst is smaller than 20 m²/g, the catalyst activity will be low; but if larger than 1,000 m²/g, the bulk density of the polymer produced will be low. The transition metal content of the polymerization catalyst may fall generally between 0.001 and 1 g, but preferably between 0.001 and 0.1 g per 100 g of the carrier in the catalyst. If the transition metal content oversteps the defined range, the catalyst activity will be low. With the catalyst held on the carrier, olefin polymers having a high bulk density and a desired particle size distribution can be obtained, and they are favorable to industrial use.

[0079] The component (A), the component (B) and optionally the component (C) and/or a carrier may be contacted with each other in an inert gas such as nitrogen, in a hydrocarbon solvent such as pentane, hexane, heptane, toluene or cyclohexane. The temperature at which they are contacted with each other may fall between -30°C and the boiling point of the solvent used, but preferably between -10°C and 100°C, and the time for their contact may fall generally between 30 seconds and 10 hours. After having been thus contacted with each other, the resulting solid catalyst component may be or may not be washed. In the contact treatment, any of the two different types of transition metal compounds for the component (A) may be used previously to the other, or the two may be mixed before they are contacted with other components.

[0080] The catalyst thus prepared may be subjected to solvent removal from it, and the resulting solid may be used for polymerization; or it may be directly used for polymerization as it is.

[0081] In the invention, if desired, the treatment of contacting at least one of the component (A) and the component (B) with a carrier so that it is held on the carrier may be effected in a polymerization system. In this case, the intended catalyst is formed in the polymerization system. For example, at least one of the component (A) and the component (B), and a carrier and optionally an organoaluminium compound for the component (C) are added to a polymerization system in which an olefin is pre-polymerized to give the intended catalyst. The olefin for pre-polymerization may be

any of ethylene and α -olefins having from 3 to 20 carbon atoms, such as propylene, 1-butene-, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene and 1-tetradecene. Of those, preferred are ethylene and propylene optionally combined with an α -olefin to be used in ethylene-propylene polymerization. The pre-polymerization may be effected in an inert hydrocarbon solvent. Concretely, the solvent may be the same as that used in preparing the solid catalyst component. The amount of the catalyst component to be pre-polymerized may fall generally between 10^{-6} and 2×10^{-2} mols/liter (solvent), but preferably between 5×10^{-5} and 10^{-2} mols/liter (solvent) in terms of the transition metal in the component. In one gram of the carrier used, the atomic ratio of aluminium in the organoaluminium compound such as methylaluminoxane (this is referred to as MAO) to the transition metal in the catalyst component, Al/transition metal, may fall generally between 10 and 5,000, but preferably between 20 and 1,000. The atomic ratio of the aluminium atom in the organoaluminium compound optionally used herein to the aluminium atom in MAO may fall generally between 0.02 and 3, but preferably between 0.05 and 1.5. The temperature for the pre-polymerization may fall between -20 and 60°C , but preferably between 0 and 50°C . The time for the pre-polymerization may fall between 0.5 and 100 hours, but preferably between 1 and 50 hours or so. In the invention, it is desirable that the catalyst is prepared through such olefin pre-polymerization.

[0082] Next described is a method of using the polymerization catalyst prepared in the manner as above in propylene homopolymerization or propylene copolymerization with ethylene and/or an α -olefin having from 4 to 20 carbon atoms.

[0083] The polymerization method is not specifically defined, to which is applicable any mode of slurry polymerization, vapor-phase polymerization, bulk polymerization, solution polymerization or suspension polymerization. However, preferred are slurry polymerization and vapor-phase polymerization; and more preferred is vapor-phase polymerization.

[0084] The polymerization condition is described. The polymerization temperature may fall generally between -100 and 250°C , but preferably between -50 and 200°C , more preferably between 0 and 130°C . The ratio of the starting monomer to the catalyst preferably falls between 1 and 10^8 , more preferably between 100 and 10^5 , in terms of the molar ratio of monomer/component (A). The polymerization time may fall generally between 5 minutes and 10 hours; and the reaction pressure preferably falls between normal pressure and 20 MPa-G, more preferably between normal pressure and 10 MPa-G.

[0085] For controlling the molecular weight of the polymers to be produced, the type and the amount of the catalyst components to be used and the polymerization temperature will be suitably selected. If desired, hydrogen may be introduced into the polymerization system for that purpose.

[0086] The polymerization solvent, if used, includes aromatic hydrocarbons such as benzene, toluene, xylene, ethylbenzene; alicyclic hydrocarbons such as cyclopentane, cyclohexane, methylcyclohexane; aliphatic hydrocarbons such as pentane, hexane, heptane, octane; and halogenohydrocarbons such as chloroform, dichloromethane. One or more such solvents may be used either singly or as combined. As the case may be, the starting monomers such as α -olefins will act also as the solvent. In some polymerization modes, no solvent will be used.

[0087] Prior to polymerization, the polymerization catalyst may be subjected to pre-polymerization. For pre-polymerizing it, for example, a small amount of an olefin may be contacted with the solid catalyst component, and the method of pre-polymerization is not specifically defined and may be effected in any known manner. The olefin to be used in the pre-polymerization is not specifically defined, and any one mentioned hereinabove may be used. For example, usable are ethylene, α -olefins having from 3 to 20 carbon atoms, and their mixtures. However, it is desirable that the olefin for the pre-polymerization is the same as that for the final polymerization to give final polymers.

[0088] The temperature for the pre-polymerization may fall generally between -20 and 200°C , but preferably between -10 and 130°C , more preferably between 0 and 80°C . A solvent may be used for the pre-polymerization, and it includes inert hydrocarbons, aliphatic hydrocarbons, aromatic hydrocarbons, and monomers. Of those, especially preferred are aliphatic hydrocarbons. As the case may be, the pre-polymerization may be effected in the presence of no solvent.

[0089] Preferably, the pre-polymerization condition is so controlled that the pre-polymerization product has an intrinsic viscosity $[\eta]$ (measured in tetralin at 135°C) of at least 0.2 dl/g, more preferably at least 0.5 dl/g, and that the amount of the pre-polymerization product falls between 1 and $10,000$ g, more preferably between 10 and $1,000$ g, relative to one mmol of the transition metal component in the catalyst.

[0090] In co-polymerization, the order of feeding the starting monomers to the reactor is not specifically defined. Preferably, however, α -olefins are fed thereto prior to propylene thereto. When ethylene is co-polymerized with propylene, it is desirable that a mixed gas of propylene and ethylene is fed to the reactor. The amount of the comonomer to be used is as follows: When an α -olefin is used as the comonomer, its amount falls between 1 and $10,000,000$ mols, preferably between 1 and $1,000,000$ mols, more preferably between 1 and $100,000$ mols per mol of the catalyst. For ethylene, the molar ratio of ethylene/propylene falls between $0.01/100$ and $99/100$, preferably between $0.01/100$ and $55/100$, more preferably between $0.01/100$ and $10/100$.

3. Moldings:

[0091] The moldings of the invention are obtained by molding the propylene polymer mentioned hereinabove. The

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/04142

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁷ C08F 10/06, C08F 4/64		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) Int.Cl ⁷ C08F 10/00-10/14		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Jitsuyo Shinan Toroku Koho 1996-2000 Kokai Jitsuyo Shinan Koho 1971-2000 Toroku Jitsuyo Shinan Koho 1994-2000		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) CAS ONLINE		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 11-130807, A (Idemitsu Petrochem Co., Ltd.), 18 May, 1999 (18.05.99), Claims (Family: none)	1-11
X	EP, 818458, A1 (IDEMITSU KOSAN COMPANY LIMITED), 14 January, 1998 (14.01.98), Claims; implementation example & WO, 96/30380, A1	1-11
X	JP, 6-329726, A (Ube Industries, Ltd.), 29 November, 1994 (29.11.94), Claims; implementation example (Family: none)	1, 7
X	JP, 8-231640, A (Hoechst Aktiengesellschaft), 10 September, 1996 (10.09.96), comparison example 1 (C1) & EP, 719802, A2 & DE, 4446923, A	1, 7
A	US, 5708101, A (John E. Bercaw et al), 13 January, 1998 (13.01.98), Claims (Family: none)	1-11
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 04 September, 2000 (04.09.00)		Date of mailing of the international search report 12 September, 2000 (12.09.00)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/04142

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, 721954, A1 (IDEMITSU KOSAN CO., LTD.), 17 July, 1996 (17.07.96), Claims & WO, 95/09172, A1 & CA, 2172635, A & US, 5854165, A	1-11
PA	WO, 99/67303, A1 (Idemitsu Petrochem Co., Ltd.), 29 December, 1999 (29.12.99), Claims; implementation example & JP, 11-166084, A & JP, 11-302474, A & JP, 2000-95820, A	1-11

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